radii given in Ref. 1 are about 2% too large, and that the double-bond carbon–oxygen distance should be 1.26 Å.) The only other available value for the carboxyl group, aside from the value 1.29 ± 0.05 Å reported in the following paper for the acetate group, is C–O = 1.25 ± 0.05 Å for crystalline oxalic acid dihydrate.[7] It seems probable that this value is slightly low, especially since the value 1.59 ± 0.07 Å reported for the bond between the two carboxyl carbon atoms is about 0.10 Å higher than the value expected for a single carbon-carbon bond serving as the path of conjugation for two double bonds. Moreover, it seems probable that the value C–O = 1.24–1.27 Å reported for the carbonate ion in various crystals is somewhat low, inasmuch as the distance for resonance of one double and two single bonds would be expected to be somewhat larger than that for one double and one single bond, as in the carboxyl group. An accurate redetermination of the parameter for these crystals should be made.

We are indebted to Dr. S. Weinbaum for many of the calculations involved in this investigation.

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[2] L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 606 (1933).
[3] A. S. Coolidge, *Jour. Am. Chem. Soc.*, **50**, 2166 (1928); **52**, 1874 (1930).
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[6] W. M. Latimer and W. H. Rodebush, *Jour. Am. Chem. Soc.*, **42**, 1419 (1920).
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THE STRUCTURE OF THE CARBOXYL GROUP. II. THE CRYSTAL STRUCTURE OF BASIC BERYLLIUM ACETATE

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The crystal structure of basic beryllium acetate, $Be_4O(CH_3COO)_6$, has been studied by Bragg and Morgan,[1] who reported some spectrometric intensity measurements and showed the cubic unit of structure to have $a_0 = 15.72$ Å and to contain eight molecules, and by Morgan and Astbury,[2] who showed the space group to be T_h^4. In neither study was the atomic arrangement determined. We have found an atomic arrangement which accounts satisfactorily for the data of these authors and for additional intensity data obtained photographically, and which provides information regarding the structure of the acetate group.

The crystals used, which were kindly prepared for us by Dr. G. W. Wheland, were in the form of octahedra several millimeters in diameter. Laue and oscillation photographs were made and interpreted in the usual way. Layer-line separations on these led to the value $a_0 = 15.8 \pm 0.1$ Å for the edge of the unit, in agreement with the value reported by Bragg and Morgan. It was also found that a Laue photograph on (111) showed a three-fold axis but no symmetry planes, and that no reflections of the types $\{hkl\}$ with $h + k$ odd and $\{hk0\}$ with $^1/_2(h + k)$ odd occurred, verifying Morgan and Astbury's choice of T_h^4 as the space group.

The complexity of the possible atomic arrangements based on T_h^4 makes a rigorous structure determination impractical. However, the volatility of the substance and its solubility in non-ionizing solvents suggest that the crystal contains discrete molecules, which are required by the space group T_h^4 to have the point-group symmetry T. As suggested by the previous investigators, a reasonable type of structure for the molecule is that shown in figure 1. Each beryllium atom (or ion) is surrounded by four oxygen atoms at the corners of an approximately regular tetrahedron, as in beryllium oxide. The electrostatic valence rule is satisfied, assuming, each carboxyl oxygen to be held to carbon by a resonating single-double bond. (The symmetry of the crystal requires the two oxygen atoms to be equivalent.) This structure may be described in the following way, using Wyckoff's tabulation of the results of the theory of space groups:

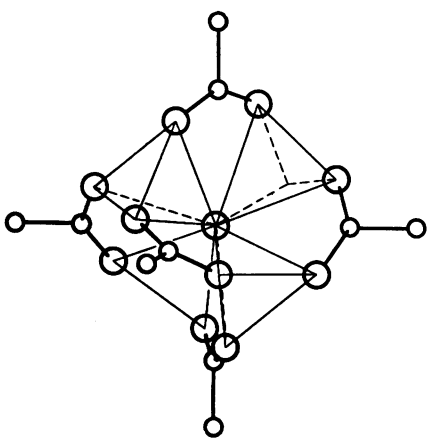

FIGURE 1

The arrangement of atoms in the molecule of $Be_4O(CH_3COO)_6$. Small circles represent carbon atoms, large circles oxygen atoms. The beryllium atoms occupy the centers of the four tetrahedra. One of the six acetate groups is not shown.

8	O_I in	8f:	000, etc.;
32	Be in	32b:	*uuu*, etc.;
96	O_{II} in	g:	*xyz*, etc.;
48	C_I in	48c:	*v*00, etc.;
48	C_{II} in	48c:	*w*00, etc.

The six parameters cannot be rigorously evaluated by use of the x-ray data alone. We consequently resort to a treatment involving the elimination of some of them by invoking a few well-founded assumptions. The

first assumption we make is that the distance between the two carbon atoms of an acetate group is the single-bond distance, 1.54 Å. This requires the relation $w - v = 0.098$ to hold between w and v. Second, we assume the Be–O distance to be 1.65 Å, as in BeO itself. This fixes the value of u as ± 0.0605, and in addition introduces a relation among the variables x, y and z, by means of which x can be determined for given values of y and z. Third, the carbon–oxygen distance in the carboxyl group is given the value 1.29 Å found for formic acid by electron diffraction.[3] These assumed values, according to previous experience, can hardly be in error by more than one or two per cent.

The problem in this way having been reduced to one involving only two parameters, which may be taken as the angle α between the carbon–oxygen bonds in the carboxyl group and the coördinate z determining the azimuthal orientation of the acetate groups, values of the intensity of reflection of x-rays from various planes were calculated according to the formula

$$I = \text{Constant} \cdot \frac{1 + \cos^2 2\vartheta}{2 \sin 2\vartheta} \cdot F^2 \cdot e^{-1.2/\sin\vartheta},$$

in which the structure factor F has its usual form

$$F_{hkl} = \sum_i f_i e^{2\pi i(hx_i + ky_i + lz_i)}.$$

Pauling-Sherman f-values[4] were used. The value 1.2 given for the exponent in the temperature factor was estimated from the angle at which a general rapid decrease in intensity of reflection sets in on oscillation photographs. Pronounced disagreement with the observed intensity values was found everywhere except in the region near $\alpha = 125°$ and $z = -0.04$, with $u = -0.0605$. No suitable range was found for the positive value of u. Calculated values of the intensity for various planes for $\alpha = 120°$, $125°$ and $130°$ and $0.03 \leqslant -z \leqslant 0.05$ are shown in figure 2. The intensity values observed by us and reported by Bragg and Morgan agree in the equality of $\{800\}$ and $\{444\}$ and the somewhat greater intensity of $\{555\}$. (Our intensity values are estimates made by visual comparison of photographs taken under identical conditions except for variation in the time of exposure.) It is seen from the figure that these relations require α to be nearly equal to $125°$ and z to -0.038. There are also in the figure intensity curves as a function of α for that value of z (-0.038, -0.038 and -0.042, respectively) for each value of α which causes the ratio $\{555\}/\{444\}$ to agree with observation. From this it is seen that the angle α is restricted by the observed equality of $\{800\}$ and $\{444\}$ to the value $124° \pm 3°$.

The correctness of the structure is supported by the general agreement

between observed and calculated intensities shown in table 1. The

TABLE 1

COMPARISON OF CALCULATED AND OBSERVED INTENSITIES OF REFLECTION FOR $Be_4O(CH_3COO)_6$

{hkl}	I CALCULATED	I OBSERVED PS	I OBSERVED BM	{hkl}	I CALCULATED	I OBSERVED PS	I OBSERVED BM
111	520	400	300	311	22	30	35
222	140	140	110	331	80	65	55
333	1.2	0	Trace	422	105	130	55
444	27	30	35	620	10	15	20
555	36	40	45	442	0.8	0	
666	0	0		446	22	25	
777	2.4	2		662	3.3	4	
888	8.7	10	10	664	0.6	0	
400	400	300	220	511	0.0	0	Trace
800	27	30	35	533	8.7	10	
220	0.6	0	Trace				
440	55	55	55				

observed values for very strong reflections are somewhat smaller than the calculated values; this we attribute to primary extinction, which seems

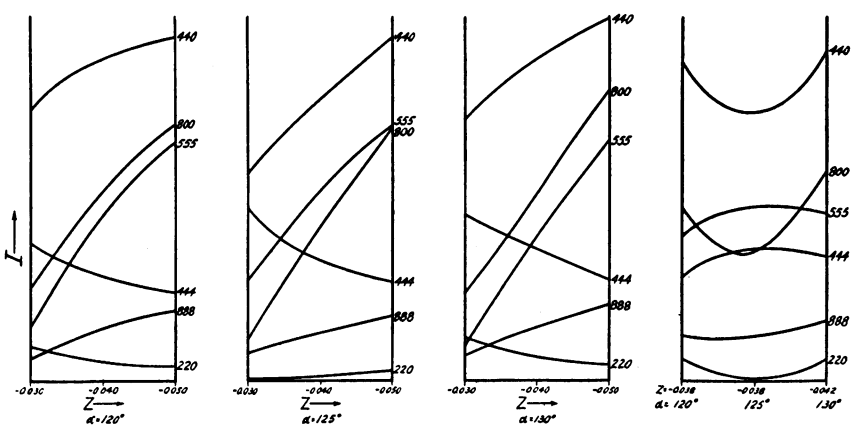

FIGURE 2

Calculated intensities for various reflections as functions of the parameters α and z.

to have been more significant for Bragg and Morgan's crystals than for ours. The remaining small discrepancies may be due to small errors in the f-values, the temperature factor or the parameters. Only for one form, $\{422\}$, do our observations show a pronounced deviation from the values of Bragg and Morgan. The calculated intensity for this reflection suggests that Bragg and Morgan's value is low.

The parameter values corresponding to the finally-chosen atomic arrangement are:

$$x = -0.163 \qquad u = -0.0605$$
$$y = -0.064 \qquad v = 0.197$$
$$z = -0.038 \qquad w = 0.295.$$

The calculated intensity values are sensitive functions of these parameters, and an arbitrary variation of as much as 0.003 impairs the agreement with observed intensities (Fig. 2). The corresponding interatomic distances may hence be considered to be verified by experiment to within about 0.05 Å.

TABLE 2

INTERATOMIC DISTANCES IN $Be_4O(CH_3COO)_6$

ATOM	NEIGHBORS IN SAME ACETATE GROUP	NEIGHBORS IN SAME MOLECULE	NEIGHBORS IN OTHER MOLECULES
Carboxyl carbon, C_I	1 C_{II} at 1.54 Å 2 O_{II} at 1.29	1 O_I at 3.10 Å 2 O_{II} at 3.36 2 O_{II} at 3.71	4 C_{II} at 4.08 Å 4 C_I at 4.10 2 C_I at 4.38 2 O_{II} at 3.52 2 O_{II} at 4.04
Methyl carbon, C_{II}	1 C_I at 1.54 Å 2 O_{II} at 2.39	2 O_{II} at 4.48 Å	4 C_{II} at 4.06 Å 4 C_I at 4.08 2 O_{II} at 3.22 2 O_{II} at 3.62
Central oxygen, O_I:		12 O_{II} at 2.80 Å 6 C_I at 3.10	
Carboxyl oxygen, O_{II}:	1 C_I at 1.29 Å 1 O_{II} at 2.35 1 C_{II} at 2.39	2 O_{II} at 2.55 Å 1 O_I at 2.80 2 O_{II} at 3.87 2 O_{II} at 4.39 1 C_I at 3.36 1 C_I at 3.71 1 C_{II} at 4.48	2 O_{II} at 3.87 Å 2 O_{II} at 4.04 1 C_I at 3.52 1 C_I at 4.04 1 C_{II} at 3.22 1 C_{II} at 3.62

The structure may be described in the following way. It contains molecules as shown in figure 1, consisting of four BeO_4 tetrahedra with one common corner. The remaining corners are occupied by oxygen atoms of the acetate groups. The distance Be–O is 1.65 Å. The tetrahedra are slightly distorted, with three edges 2.80 Å and three 2.55 Å in length, the longer edges extending from the central oxygen atom. In the acetate group the angle α has the value 124° ± 3°, equal to the value 125° ± 5° found for formic acid; we may conclude that this value of the bond angle in the carboxyl group is probably retained in all aliphatic acids.

The arrangement of the centers of the molecules in the crystal is that corresponding to the diamond structure. Each molecule is surrounded tetrahedrally by four molecules. If we consider a molecule as roughly tetrahedral in shape with similar orientation to the tetrahedron formed by the four beryllium atoms, then the adjacent molecules are so oriented as to present tetrahedral faces to one another.

Interatomic distances for carbon and oxygen atoms in the crystal are given in table 2 (up to 4.5 Å). It is seen that the molecules pack snugly together, each methyl and carboxyl carbon and carboxyl oxygen atom having eight or twelve neighbors in adjacent molecules at distances between 3.22 and 4.10 Å.

[1] W. H. Bragg and G. T. Morgan, *Proc. Roy. Soc.*, **A104**, 437 (1923).
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[3] Linus Pauling and L. O. Brockway, these PROCEEDINGS, **20**, 336 (1934).
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*NEGLECTED FACTORS IN THE DEVELOPMENT OF THERMAL SPRINGS**

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Read before the Academy, Tuesday, April 24, 1934

1. *Introduction.*—Whether or not *all* thermal springs are due to the same general conditions, all groups that I have studied in the Western United States appear to be the result of the same fundamental causes, namely: a body of circulating ground water, heated by rising jets of magmatic steam, and deriving its dissolved mineral matter partly from the adjacent rock and partly from magmatic sources. Yet great differences, not only in physical character, but in the composition of waters and gases, and in the nature of the deposits, are found in springs of the same district, sometimes in groups side by side. It is to these local factors, which differentiate hot spring groups into distinctive types, that I would invite your attention today.

2. *Factors Responsible for the Deposition of Calcium Carbonate.*—Hot springs depositing calcium carbonate (travertine), exclusively, are probably always associated with limestone. A general characteristic of thermal springs is their more or less steady yield of volcanic gases, chiefly carbon dioxide in most places. The solution of limestone by water charged with carbon dioxide and its precipitation when the gas escapes are facts familiar to all.